

PATENT ABSTRACTS OF JAPAN

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(54) LEADLESS ELECTROCONDUCTIVE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a composition, comprising a thermoplastic resin, an electroconductive fiber and a specific low-melting metal in a specific proportion, capable of retaining electromagnetic wave shielding effects, excellent in long-term characteristics and environmental compatibility without eluting lead and useful as housings, etc., of various electronic devices.

SOLUTION: This leadless electroconductive resin composition comprises (A) 30-98wt.% thermoplastic resin such as a polyphenylene ethereal resin, a polystyrene-based resin, an acrylonitrile-butadienestyrene resin, a polycarbonate resin or a blended material thereof, (B) 1-50wt.% electroconductive fiber such as a metallic fiber (e.g a copper fiber, a brass fiber, a stainless steel fiber, an aluminum fiber or a nickel fiber) and (C) 0.1-30wt.% low-melting metal without containing lead (e.g. an In-Sn alloy, an In-Bi alloy or an Sn-Ag alloy) and, as necessary, further (D) a flux in an amount of 0.1-10 pts.wt. based on 100 pts.wt. component C.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a conductive resin composition and its Plastic solid. In detail The housing and inner components of an electronic device, such as a microcomputer and a cellular phone, A conductive resin composition and Plastic solids, such as light electric appliance machines, such as housing of electrical household appliances and electrical equipment, such as television, video, radio, and an air-conditioner, housing of an inner component and a liquid crystal display, and an inner component, and electronic equipment, are started.

[0002]It is used the optimal especially as electro-magnetic interference sealed materials.

[0003]

[Description of the Prior Art]Although the charge of an electromagnetic wave shielding material is used for the inner component exterior parts of various electrical and electric equipment, etc., about the microcomputer, it spreads splendidly in recent years and is used for an increasingly wide range of fields. In order that the microcomputer may contain the high frequency transmitter as an object for clock signal generating and may treat a pulse form wave again, it does disturbance to electronic equipment, such as surrounding television, each transmitter, etc., including [therefore] a high frequency component mostly.

[0004]On the other hand, many of microcomputers are portable types.

Although it can carry and install anywhere, a computer circuitry is directly put to the strong pulse form electric wave (for example, thing to generate by spark discharge) generated from surrounding apparatus etc. depending on the conditions installed, and, thereby, a computer malfunctions.

Although it takes into consideration in electric circuit as this measure in view of these situations, radiation of an unnecessary electric wave is lessened and the policy which make

influence of an outside pulse hard to be influenced is taken, there is a limit also in this and giving an electromagnetic wave screening effect to the housing which surrounds a microcomputer too is performed. As such housing, many things made of thermoplastics are used also in it from a viewpoint of mass production nature, the flexibility economical efficiency of a design, and lightweight nature, and many policies are performed in order to give this electromagnetic wave cover nature.

(1) Provide a conductive electromagnetic wave shielding layer in inner and the outside surface of a thermoplastics Plastic solid by methods, such as plating, paint, thermal spraying, and foil adhesion.

(2) Equip the molding die with the substance which has an electromagnetic wave screening effect of a wire gauze, a metallic foil, etc. beforehand, unify by the molding operation of thermoplastics and acquire an electromagnetic wave cover nature Plastic solid.

(3) Fabricate with the thermoplastics which mixed conductive substances, such as a metal powder, carbon powder, a metallic foil, a metal fiber, and carbon fiber, and acquire an electromagnetic wave cover nature Plastic solid.

[0005]However, among these policies, about the method of (1), in order to raise the adhesion strength of a thermoplastics Plastic solid and an electromagnetic wave shielding layer, use of an expensive material and introduction of expensive equipment were needed. About the policy of (2), in order that layers, such as a wire gauze, might prevent movement by flow of the synthetic resin which the forming cycle plasticized, modification, and a fracture, introduction of expensive equipment was needed.

[0006]On the other hand, when the policy of (3) mixes metal, carbon fiber, and a flake, it is a well-known fact that it is effective for especially improvement in an electromagnetic wave screening effect. However, the further improvement in the reliability of the characteristic was required over a long period of time. The master pellets of the pellet type which carried out encased type Seiichi embodying of the thermoplastic resin layer to the surface of the conductivity bulking agent which changes from copper textiles and a low melting point metal to JP,6-47254,B, for example in order to solve this, The invention of the conductive resin composition blending a thermoplastic resin pellet is indicated. According to the example and comparative example of this invention, by scoring Sn60% and Pb40% of low melting point metal, the electromagnetic wave shielding effect after 80 **x 3000-hour progress is improved, and it is. To JP,60-189106,A, thermoplastics and nickel, The continuous glass fiber-like conductivity bulking agent which has metal plating layers, such as tin and a solder alloy, is used as the main ingredients, and there is a statement about the conductive molding material in which the loadings of the continuous glass fiber-like conductivity bulking agent which has said metal plating layer are characterized by being 5 to 40 % of the weight to thermoplastics. In addition, various proposals are made about the low melting point metal which contains lead as

an ingredient.

[0007]However, since lead has a possibility of it being eluted by acid rain etc. and polluting groundwater etc. when it is discarded, by the industrial waste method, it is obliged to discard to the disposal field made from concrete intercepted when not less than 3 ppm lead was detected by the elution test. When lead is taken in from a digestive organ or a breather and is accumulated, it has a possibility of being poisoned. The damage of acid rain is serious in each country, and the damage is reported by Japan which is alkaline soil in recent years.

[0008]

[Problem(s) to be Solved by the Invention]There is a technical problem of this invention in providing conductive resin Plastic solids which are high, are excellent also in the characteristic over a long period of time, and do not have leaden elution, such as a light electric appliance machine and electronic equipment. [of an electromagnetic wave screening effect]

[0009]

[Means for Solving the Problem]That is, this invention relates to 0.1 to 30 % of the weight of low melting point metals which do not contain the (A) thermoplastics 30 - 98 % of the weight and the (B) conductive fiber 1 - 50 % of the weight and (C) lead, a conductive resin composition, ** and others, and its Plastic solid, in injection molding of thermoplastics.

[0010]This invention is explained in detail below. As thermoplastics used for this invention, thermoplastics, such as polyphenylene ether system resin, polystyrene system resin, ABS plastics, polycarbonate resin, polyamide resin, polyethylene resin, polypropylene resin, and polyvinyl chloride resin, can be mentioned.

[0011]Mixed material etc. which made these resin a subject can be used for this invention. For example, mixed material of polystyrene resin, polycarbonate resin, and ABS plastics which blended polyphenylene ether can be used good. An injection-molded product of these resin has very good balance of performance and economical efficiency, and it is suitable for it in housing. Various reinforcements and various packing can be blended with these resin. For example, one sort, such as glass fiber, a glass flake, a glass bead, asbestos, calcium carbonate, and wood flour, or two sorts or more can be blended with the above-mentioned resin.

[0012]It is more preferred that fire retardant is included in these resin, and an organophosphorus compound, an inorganic phosphorus compound, magnesium hydroxide, aluminium hydroxide, a halogenated compound, etc. are mentioned. As an example of an organophosphorus compound, phosphoric ester, phosphite, phosphine, phosphine oxide, a BIHOSU fin, phosphonium salt, phosphinate, etc. are mentioned. As an example of an inorganic phosphorus compound, an inorganic system phosphate etc. which are represented by ammonium polyphosphate etc. are mentioned.

[0013]As a conductive filler mixed into thermoplastics used for this invention, A metal fiber, a

metallic foil, metal flakes, a metal powder, carbon powder, carbon fiber, metal plating, metal deposition, carbon fiber that carried out metallizing or glass fiber, mica which performed metal plating, organic textiles processed with a conductive substance, etc. can be mentioned. As a conductive filler, a metal fiber is preferred.

[0014]As an example of a metal fiber, copper textiles, brass textiles, a stainless steel fiber, aluminum textiles, a nickel fiber, etc. are mentioned, and these can be obtained by methods, such as a wire-drawing drawing method, a melt spinning method, the coil strip cutting method, the chatter oscillating cutting method, and the wire cutting method. What carried out the surface treatment of these metal fibers by a titanate coupling agent etc. may be used.

[0015]Content of these conductive fibers is 5 to 35 % of the weight still more preferably three to 40% of the weight preferably one to 50% of the weight. It is added suitably if needed for conducting performance. A low melting point metal which does not contain lead used in this invention refers to 400 °C or less of metal simple substances which have the melting point of 350 °C or less still more preferably and mixtures preferably. [500 °C or less of] In it, a thing which does not contain lead is pointed out and lead, mercury, cadmium, thallium, and arsenic are not included preferably.

[0016]That is, it is an alloy expressed with Sn, Bi, Zn, In simple substance and a Sn-A-X-Y system, and an In-A-X system. (A is In, Bi, Ag, Cu, Sb, Zn, Au, etc. here, and X and Y are Ag, Cu, In, Bi, Sb, etc., when not adding or adding.)

As an example, Sn simple substance, Bi simple substance, a Zn simple substance, a Sn-Bi-X system, a Sn-In-X system, a Sn-Ag-X system, a Sn-Bi-X system, a Sn-Zn-X system, a Sn-Ag-X system, a Sn-Sb-X system, etc. can be raised. Here, nothing adds or X means addition of other metal. these metal -- inner -- good -- better -- those of a potato is a Sn-Bi-X system, a Sn-In-X system, a Sn-Ag-X system, a Sn-Bi-X system, a Sn-Zn-X system, a Sn-Ag-X system, and a Sn-Sb-X system.

[0017]If an example of these low melting point metals is given still more concretely, 48Sn-52In (melting point of 117 °C), 43Sn-57Bi (melting point of 139 °C), and Sn-Ag₂₂₀ (96.5Sn-3.5Ag) (melting point of 221 °C), for example, the Senju metal industry stock company product watch. Sn-Cu₂₃₀ (melting point of 227 °C), for example, the Senju metal industry stock company product watch. Sn-Ag-Cu (Bi, Sb), for example, Senju metal industry stock company product watch 7027 (melting point of 216-220 °C) Senju metal industry stock company product watch 7047 (melting point of 216-323 °C) Sn-Ag- Sn-Sb-Cu₉₀₂₈ (232-321 °C), for example, the Senju metal industry stock company product watch. 97In-3Ag (melting point of 143 °C), Sn-In- (Ag, Cu), Sn-Bi- (Ag, Cu, In)7046, for example, Sn-Ag-Bi-Cu Senju metal industry stock company product watch, Sn-Zn- (In, Bi, Ag), Sn-Ag- (Bi, Sb, Cu) and 50Sn-50Sb (melting point of 235-240 °C), 20Sn-80Au (280 °C), etc. can be raised. These metal and an alloy are independent, or are combined two or more kinds, and are used. Other metal may be contained as 5% or less of

a minor constituent. These are only illustration and it is a right category of this application which does not contain lead with a low melting point metal. Since it comes out, it is clear that what used these things as a base and added minor constituents other than lead is included in a range. shape of these low melting point metals -- a grain, a line, and powder state -- cylindrical -- any may be sufficient.

[0018]An addition of these low melting point metals is 1 to 10 % of the weight still more preferably 0.5 to 20% of the weight preferably 0.1 to 30% of the weight. It is not desirable in order for a low melting point metal to separate and to spoil physical properties and appearance of resin, if it adds exceeding 30 % of the weight. With flux used in this invention, stearic acid of an organic acid system, lactic acid, oleic acid, glutamic acid, lauryl acid, rosin of a resin system, activity rosin, vegetable rosin, fats and oils, etc. which are generally used are mentioned. Since flux containing halogen causes metallic mold corrosion etc., it is not preferred. In this invention, Flach is an optional component. When blending staple fiber RAKKUSU, 1-8 weight-section addition is preferably carried out 0.1 to 10 weight section to low melting point metal 100 weight section.

[0019]In the range which does not spoil the feature, in accordance with a publicly known method, it can add in a resin composition of this invention suitably, and various kinds of stabilizer, a plasticizer, lubricant, fire retardant except having illustrated, paints, an inorganic bulking agent, etc. can be used for it. To use an electrical conducting material in this invention as electro-magnetic interference sealed materials, it is required for there to be an electromagnetic wave screening effect of not less than 10 dB at least, and there needs to be not less than 20 dB of not less than 30 dB still more preferably preferably.

[0020]As an example of use of a concrete material of a conductive material of this invention, it is [circuit / housing, such as medical equipment which has television, a cellular phone, a personal computer, family computer a game machine, an air-conditioner, a copying machine, a microwave oven, and an electronic circuit an inner component, and] suitable for wrap material etc. in electronic equipment of cars, such as a wrap member. Sheet forming including shaping by an injection molding machine which the necessity in particular for limitation does not have about a method of fabricating an electromagnetic wave shielding member, and is usually performed from a resin composition of this invention or a method by a melting press, vacuum forming, and multilayer shaping are used. What is necessary is just this invention in a stage of mold goods also about a raw material, and a low melting point metal may be used for thermoplastics and a conductive fiber, mixing simply, A low melting point metal may be mixed with thermoplastics/conductive fiber, and it may be used, and may be used, mixing a conductive fiber/low melting point metal, and a thermoplastic fiber, Thermoplastics/low melting point metal may be mixed with thermoplastics/conductive fiber, and it may be used, and may be used, mixing thermoplastics / conductive fiber / low melting point metal, and thermoplastics,

and thermoplastics may be used for thermoplastics / conductive fiber / low melting point metal, and thermoplastics/conductive fiber, mixing. Under the present circumstances, as an example of the methods of production of thermoplastics/conductive fiber, thermoplastics/low melting point metal, a thermoplastic fiber / conductive fiber / low melting point metal, etc., etc., a conductive fiber made into the shape of a successive line by a thermoplastic fiber -- and -- or it being able to granulate by cutting, after covering a low melting point metal fiber, and, A conductive fiber is bundled with a method and a low melting point metal which mix and use a pellet of this and thermoplastics, this can be cut and a method of mixing with a pellet of thermoplastics and using, etc. can be mentioned.

[0021]

[Embodiment of the Invention]The measuring method used for the example is explained.

[1] In a radio wave dark box using the measurement ANRITSU CORP. make Specht ROANA riser MS623A measuring instrument of an electromagnetic wave shielding effect, and tracking generator MH628A with a 100x100x2-mm monotonous specimen. It measures from the frequency 100 in a 1000-MHz frequency range, and expresses with the attenuation value of 500 MHz.

[2] Measure electromagnetic wave shielding by dB like **, and express with the retention, after putting the measurement mold goods of the characteristic into the constant temperature/humidity chamber of the temperature of 70 **, and 70% of humidity and exposing them for 100 days over a long period of time.

[3] Grind elution test mold goods for a chip (1 mm - 2 mm), mix this with an eluate at a rate of 10% of a weight ratio, and measure the quantity of the lead which shook continuously for 6 hours and was eluted with the shaker with an atomic absorption method. The eluate used 0.1 mol of acetic acid, and the liquid which melted 0.0643 mol of sodium hydroxide in 1000 ml of pure water.

[0022]The kind and manufacturing method of raw material which are used in the example are shown below.

** Abbreviate to modified-polyphenylene-ether resin Asahi Chemical Industry Co., Ltd. make, the xyron 240Z, and PPE/PS in Table 1.

** PC/ABS (mixed material of polycarbonate resin and ABS plastics) It abbreviates to the Ube sycon incorporated company make, Phycho Roy C280, and PC/ABS in Table 1.

** HIPS (rubber strengthening polystyrene resin)

It omits the inside HIPS of Asahi Chemical Industry Co., Ltd. make and fire-resistant polystyrene VS40 and Table 1.

** It cut in diameter in terms of the yen of 30 micrometers, the method, i.e., coil strip cutting method, which are indicated to adjustment EMC 1992.11.5. <No.55> p78 of the metal fiber master pellets used by this example - 82.

[0023] Thermoplastics is covered for 500 metal fibers of each construction material of a statement, and a linear low melting point metal (the flux of a rosin system is included depending on the case of a statement among Table 1) on the surface through the dice of an extrusion machine all over Table 1. This is cut in length of 5 mm by a pelletizer in a grain direction, and it is considered as metal fiber master pellets. The low melting point metal given in Table 1 is as follows.

- #7046 : the Senju metal industry incorporated company make Lot number 7046 (Sn-Ag-Bi-Cu system; melting temperature of 189-214 **)
- #220 : the Senju metal industry incorporated company make Lot number 220 (Sn-Ag system; melting temperature of 221 **)
- #7027 : the Senju metal industry incorporated company make Lot number 7027 (Sn-Ag-Cu system; melting temperature of 216-220 **)
- #230 : the Senju metal industry incorporated company make Lot number 220 (Sn-Cu system; melting temperature of 227 **)
- Sn/Pb : the usual Sn63%-Pb37% of solder.

[0024]

[Examples 1-10] Metal fiber master pellets are mixed with each thermoplastics by the blending ratio shown all over Table 1, Using an injection molding machine (auto shot 50B FANUC, LTD. make), PC/ABS shall set PPE/PS as 270 **, and shall be set as 250 **, HIPS shall set a cylinder temperature as 240 ** respectively, a die temperature shall be 50 **, and a 100x100x2-mm monotonous specimen is fabricated. Various kinds of examinations are presented using these mold goods.

[0025]

[Comparative examples 1-3] The low melting point metal of Sn/Pb was used, and also it carried out like the example. The comparative example 1 is equivalent to Example 1 at comparative example 2 Example 9, and the comparative example 3 is respectively equivalent to Example 10.

[0026]

[Table 1]

| | | 実 施 例 | | | | | | | | | | 比 較 例 | | |
|-----------|-----|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 1 | 2 | 3 |
| 樹脂組成 | | | | | | | | | | | | | | |
| (A) 樹脂種 | | PPE/PS | PPE/PS | PC/ABS | PC/ABS | HIPS | PPE/PS | PPE/PS | PPE/PS | PPE/PS | PPE/PS | PPE/PS | PPE/PS | PPE/PS |
| 添加量 | 重量% | 78.0 | 78.0 | 78.0 | 78.0 | 78.0 | 78.0 | 78.0 | 78.0 | 76.0 | 76.0 | 78.0 | 76.0 | 76.0 |
| (B) 導電性繊維 | | 銅 | 黄銅 | 銅 | 黄銅 | 銅 | 黄銅 | 黄銅 | 黄銅 | 黄銅 | 黄銅 | 銅 | 黄銅 | 黄銅 |
| 添加量 | 重量% | 19.5 | 19.5 | 19.5 | 19.5 | 19.5 | 19.5 | 19.5 | 19.5 | 19.0 | 19.0 | 19.5 | 19.0 | 19.0 |
| (C) 低融点金属 | | #7046 | #7046 | #7046 | #7046 | #7046 | #220 | #7027 | #230 | #7046 | #7046 | Sn/Pb | Sn/Pb | Sn/Pb |
| 添加量 | 重量% | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 5.0 | 2.5 | 2.5 | 5.0 | 2.5 |
| (D) フラックス | | ロジン系 | ロジン系 | ロジン系 | ロジン系 | ロジン系 | ロジン系 | ロジン系 | ロジン系 | ロジン系 | — | ロジン系 | ロジン系 | — |
| 添加量 | 重量部 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | 0.25 | 0.00 | 0.13 | 0.25 | 0.00 |
| 特性 | | | | | | | | | | | | | | |
| 電磁波シールド効果 | dB | 52 | 50 | 53 | 54 | 47 | 48 | 50 | 49 | 52 | 49 | 53 | 50 | 48 |
| 長期特性 | % | 93 | 95 | 92 | 93 | 92 | 95 | 98 | 97 | 96 | 73 | 86 | 89 | 65 |
| 溶出試験 | ppm | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 45 | 89 | 54 |

[0027]

[Effect of the Invention] The conductive resin composition and Plastic solid of this invention hold an electromagnetic wave shielding effect, are excellent in the characteristic over a long period of time, do not have leaden elution, and are good also to environment compared with the conventional thing.

[Translation done.]